ENERGY CONSERVATION

ASSESSMENT OF THE COMPOSITIONS AND COMPONENTS FOR OBTAINING FOAM-GLASS-CRYSTALLINE MATERIALS FROM ALUMINOSILICATE INITIAL MATERIALS

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The compositions suitable for obtaining foam-glass-crystalline materials from aluminosilicate initial materials (for the example of zeolite and greenstone) by means of a dual-stage technology at temperatures not exceeding 900°C are examined. The assessment criteria for the initial materials and compositions of the glass granulate are determined. It is shown that under the established conditions aluminosilicate initial material makes it possible to obtain foam-glass-crystalline material with density $250 – 350$ kg/m^3 and compression strength up to 2 MPa.

There is now heightened interest in promising heat-insulating materials that will make it possible to effectively solve the problem of heat protection of buildings and structures. One such modern heat-insulating material is foam glass, which possesses high-insulating characteristics and is inflammable, durable, and reliable. Foam-glass-crystalline materials (FGCM) have similar properties; these materials are distinguished from foam glass by the presence of a crystalline phase.

Data on obtaining FGCM on the basis of zeolite-containing rock, known under the trade name Sibirfom, are presented in [1]. The technology which the authors propose for fabricating Sibirfom is a one-stage process which includes heat-treatment of zeolites with additives at temperatures $1180 – 1200°C$ and obtaining material with density about 650 kg/cm^3. Preliminary investigations have shown that a two-stage process for obtaining FGCM (introduction of fritting of zeolite with calcined soda as the first stage) makes it possible to decrease the technological temperature to 850°C and obtain material with bulk granular density 420 kg/m^3 [2].

It must be underscored that the quality of FGCM is largely determined by the composition of the intermediate product (glass granulate), on the basis of which this material is obtained. According to its phase composition the glass granulate is amorphous-crystalline with the glass phase predominating. There exists a general law: as the amount of the crystalline phase in the glass granulate decreases, on the whole the conditions for the mixture to transition into a pyroplastic state at the foaming stage improve and FGCM density decreases.

The objective of the our work is to determine the compositions suitable for obtaining FGCM on the basis of aluminosilicate initial material by a two-stage technology at temperatures not exceeding 900°C and to determine the criteria for evaluating the initial materials.

The analysis of the sequence of changes of the melting temperature and the choice of compositions were made by using the phase diagrams of the system $Na_2O – Al_2O_3 – SiO_2$, taking account of three factors:

the formation temperature of the liquid phase (melt) should not exceed 900°C;

the amount of the liquid phase must not be less than 70%,[2] which is necessary to ensure a pyroplastic state at the foaming stage; and,

the liquid phase should have the optimal viscosity ($10^3 – 10^6$ Pa · sec) in the foaming temperature range.

The concentration region of compositions having at least 70% melt at temperatures below 900°C is shown in Fig. 1. As one can see, the region is bounded according to the SiO_2

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[2] Here and below — content by weight.

content (57 – 75%) and the Al_2O_3 content (5 – 16%). The most easily melting eutectics of the system fall into this region:

between disilicate, albite, and nepheline with melting temperature $732 \pm 5°C$ (61.5% SiO_2, 12.5% Al_2O_3, 26.0% Na_2O);

between disilicate, albite, and silica with melting temperature $740 \pm 5°C$ (73.8% SiO_2, 4.7% Al_2O_3, 21.5% Na_2O); and,

between disilicate, nepheline, and metasilicate with melting temperature 760°C (57.9% SiO_2, 10.1% Al_2O_3, 32.0% Na_2O).

One of the most important parameters which determine the behavior of the melt during foaming is the viscosity, which lies in the range $10^3 – 10^6$ Pa · sec at temperatures corresponding to gas release. The viscosity of the silicate melt depends in a complex manner on the composition and temperature. It is acknowledged that in a wide temperature range the temperature dependence on the viscosity cannot be described by any one type of equation. The computed values of the viscosity of the melt are approximate and do not take account of all particularities of the chemical and mineral composition of the material.

The viscosity modulus characterizing the viscous properties of the melt taking account of its chemical composition was used to make a preliminary evaluation of the effect of the composition on the viscosity. The modulus is calculated on the basis of the component-effect principle: viscosity increasing components are in the numerator and viscosity decreasing components are in the denominator. The different effect of the components of the composition on the viscosity is taken into account by means of factors associated with the magnitude of the ionic radius of the cation. The larger the factor for a component, the greater the effect of this component on the viscosity is:

$$M_v = \frac{M_{SiO_2} + 2M_{Al_2O_3}}{2M_{Fe_2O_3} + M_{CaO} + M_{MgO} + 2M_{K_2O} + 2M_{Na_2O}},$$

where $M_{R_mO_n}$ is the amount of the corresponding oxides, %.

A calculation of the modulus of the viscosity of compositions that fall into the region delineated in the diagram showed a quite strong difference of the viscous properties; the modulus varies from 0.90 to 5.25. Choosing as an example the composition of the commercial container glass used in the production of foam glass — 72% SiO_2, 3% Al_2O_3, 7% CaO, 4% MgO, 14% Na_2O — with viscosity modulus 2, we narrowed the range of optimal compositions by conditional boundaries characterized by the values of the modulus 2 ± 0.2 (Fig. 2). Compositions with Al_2O_3 content 5% and SiO_2 ranging from 72 to 75% (region of disilicate and quartz fields) and with 15% Al_2O_3 and the corresponding range from 60 to 64% (nepheline and albite region) fall into the optimal viscosity range ($1.8 < M_v < 2.2$). The computed values
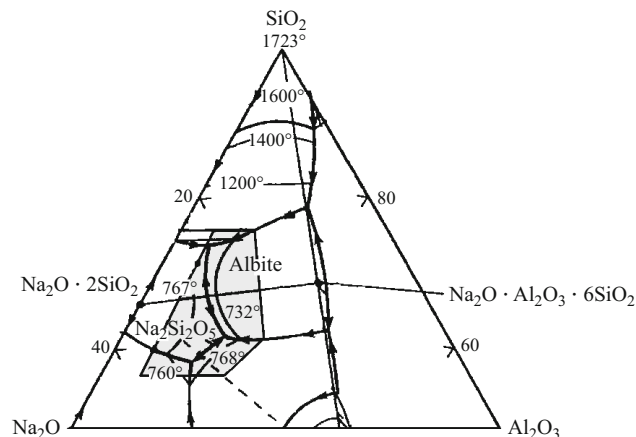

Fig. 1. Phase diagram of the system $Na_2O – Al_2O_3 – SiO_2$ [3] (the shaded region is the region of compositions which give at least 70% melt at temperatures below 900°C).

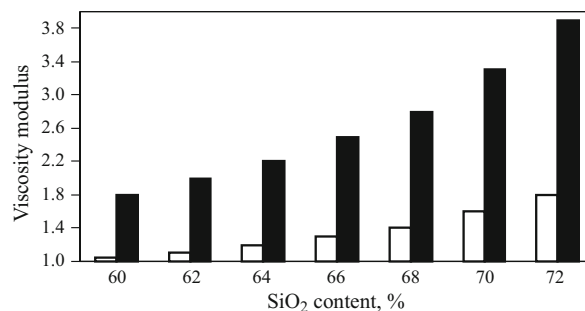**Fig. 2.** Viscosity modulus versus the SiO_2 content: $\square$) with 5% Al_2O_3 content; $\blacksquare$) with 15% Al_2O_3 content.

of the logarithm of the viscosity of the chosen compositions in the temperature interval 800 – 850°C correspond to the optimal values. Thus, the initially delineated concentration range in the region of compositions in the diagram of the system narrows to the region corresponding to the chosen values of the viscosity modulus.

To obtain the chosen compositions, aluminum silicate initial material, represented by the zeolite-containing rock of the Sakhaptinskoe deposit (Krasnoyarsk Krai) and diabase of the Barzasskoe deposit (Kemerovo Oblast'), was considered as a main component of the mixes. Chemical analysis shows the presence of different oxides, the main ones being silicon, aluminum, and alkali-earth, as well as a high content of iron oxides in diabase (Table 1). An elevated content of aluminum oxide promotes an increase of viscosity and a decrease of crystallization activity, while the iron and calcium oxides have a liquefying and fluxing effect [4].

Two three-component glass compositions, meeting all requirements listed above, with relatively low and high aluminum oxide content were chosen as an example. The computed component composition of the charge is presented in Table 2 (ShTs-1 and ShTs-2 — charges with first and second

TABLE 1.

Material	Content, wt.%							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	calcination losses
Diabase (Barzasskoe)	52.70	16.50	12.70	9.90	4.10	1.76		2.34
Zeolite (Sakhaptinskoe)	63.12	13.26	2.38	3.50	1.75	1.04	3.07	11.88

TABLE 2.

Charge	Charge composition, %				Glass composition, %			Viscosity modulus
	zeolite	soda	marshallite	diabase	SiO_2	Al_2O_3	Na_2O	
ShTs-1	38	22	40	–	72	7	21	2.2
ShTs-2	80	20	–	–	62	13	25	1.8
ShD-1	–	20	53	27	73	6	21	2.0
ShD-2	–	10	–	90	53	17	30	1.5

compositions based on zeolite, ShD-1 and ShD-2 — charges based on diabase).

The mix formulations for obtaining the glass granulate are adjusted according to the content of the alkali oxides by introducing additional sodium carbonate. The compositions of the glasses obtained from these charges were converted to three-component compositions taking account of the molecular mass of the calcium, magnesium, and iron oxides and their effect on the viscosity. It is evident that when the Al_2O_3 content is relatively low a silica-containing material must be added to the mix; marshallite, being an active, finely disperse material with a high silicon oxide content (> 95%), was chosen as such an additive. For compositions with a high Al_2O_3 content, the charge formulation is simplified to a two-component charge. However, the viscosity modulus of a composition of the glass granulate from a mix based on ShD-2 diabase is comparatively low, which does not correspond to the chosen requirements and therefore is not considered below.

The initial materials were prepared by standard methods with particles smaller than 100 μm passing completely

Fig. 3. Amount of the crystalline phase versus the treatment temperature of ShTs-1 (*1*), ShD-1 (*2*), and ShTs-2 (*3*) mixes.

through a sieve. The charge obtained was densified beforehand by rolling on a plate granulator, which makes it possible to increase its chemical activity and intensify the silicate- and glass-forming process on the one hand and to preserve the chemical uniformity, achieved at the mixing stage, in order to make the reactions to proceed more fully in each individual granule, on the other.

Granules of size 5 – 7 mm were processed in the temperature range from 750 to 900°C with the same soaking time at the maximum temperature and the amount of the residual crystal phase was determined. It was found that heat-treatment (850°C) of the three-component mix with zeolite rock makes it possible to obtain glass granulate with 5% content of the crystalline phase (Fig. 3). For a two-component mix at the same temperature, 15% crystalline phase remains in the glass granulate and, correspondingly, 10% remains for a sintered mix with diabase.

It is observed that, generally, the amount of the crystalline phase decreases with increasing temperature. Stabilization occurs when the temperature increases to 900°C, and the melt crystallizes at higher temperatures. In the melts of the present mixes, formed at temperature above 900°C, crystallization is observed to occur in the form of albite $Na_2O \cdot Al_2O_3 \cdot 6SiO_2$; this is confirmed by XPA data.

Thus, the crystalline phase is present in the lowest amounts in glass granulate obtained from a mix containing marshallite. Evidently, complicating the composition by adding a glass forming agent gives a higher degree of completion of the silicate- and glass-forming reactions.

The glass granulate obtained was comminuted to specific surface of not less than 5000 cm^2/g with the addition of a gas forming agent and foamed up. Some characteristics of the FGCM were determined and the results are presented in Table 3. Compared with the properties of foam glass, it is evident that the FGCM exhibit greater strength, which makes
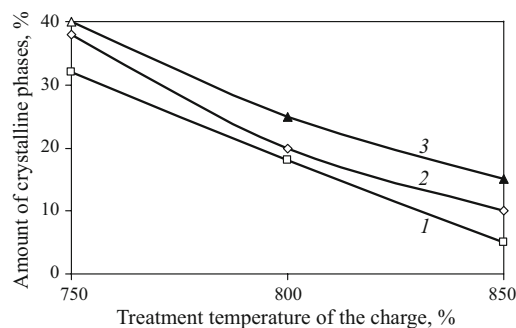
it possible to expand the range of application of these materials.

The following factors were identified as criteria for evaluating the components and compositions of the glass granulate based on aluminum silicate initial material:

to obtain glass granulate, the particle sizes of the initial material must not exceed 100 μm;

the content of the glass forming silicon oxide in the initial material must be at least 60%; for lower SiO_2 content, the mix must be adjusted by introducing an additional high-silica component;

for ratios of SiO_2 to Al_2O_3 of at least 4 in the initial material, only additional alkali-containing components are added; the mix is a two-component mixture;

the viscosity modulus of the glass granulate composition must lie in the range 2 ± 0.2; for $M_v < 1.8$ the content of the acidic component and for $M_v > 2.2$ that of the alkali component in the charge must be increased; and,

for the optimal composition of the mix, the amount of the liquid phase formed at temperatures no higher than 900°C is at least 70%.

In summary, aluminum silicate initial material satisfying all established conditions makes it possible to obtain

TABLE 3.

Indicator*	FGCM based on		Foam glass based on cullet
	zeolite	diabase	
Density, g/m^3	250	300	100 – 250
Compression strength, MPa	1.8	2.0	0.5 – 1.5

* The water absorption was no more than 10%.

foam-glass-crystalline material with density ranging from 250 to 350 kg/m^3 and compression strength up to 2 MPa.

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